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(54) ADDITIVE FOR PRODUCING PAPER

## (57)Abstract:

PURPOSE: To obtain an additive for producing paper, relatively low in viscosity in spite of containing a high mol. wt. (meth)acrylamide copolymer, excellent in workability, and exhibiting an excellent paper-reinforcing effect as an inner additive or an outer additive.

CONSTITUTION: The additive is produced from a (meth)acrylamide copolymer obtained by copolymerizing 99.9-80mol.% of (meth)acrylamide, 0.05-10mol.% of a (meth)allyl group-containing monomer selected from the group of (meth)allyl carboxylic acid, (meth)allyl sulfonic acid, their salts and (meth)allyl alcohol, 0.005-10mol.% of at least one kind selected from the group of N,N-dimethyl (meth)acrylamide, N-methyl(meth)acrylamide, N-ethyl (meth)acrylamide, N-isopropyl (meth)acrylamide and N-t-butyl(meth)acrylamide represented by formula:  $\text{CH}_2=\text{C}(\text{R}_1)-\text{CONR}_2(\text{R}_3)$  (R1 is H, methyl; R2 and R3 are H, a 1-4C alkyl), and 40wt.% of at least one kind of anionic, cationic and anionic vinylic monomers.

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CLAIMS

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[Claim(s)]

[Claim 1] (A) (meta) The monomer and (C) general formula (1): $\text{CH}_2=\text{C}(\text{R}_1)-\text{CONR}_2$  (among a formula (R3)) which have one allyl group as an acrylamide and (B) carbon-carbon double bond (meta) R1 A hydrogen atom or a methyl group, and R2 The straight chain of a hydrogen atom or carbon numbers 1-4, or the alkyl group of branched chain, R3 the alkyl group of the straight chain of carbon numbers 1-4, or branched chain -- expressing -- additive for paper manufacture which comes to contain the acrylamide system copolymer obtained by copolymerizing N-permutation (meta) acrylamides expressed (meta).

[Claim 2] (A) (meta) Monomer 0.05 - ten-mol % and (C) general formula (1): $\text{CH}_2=\text{C}(\text{R}_1)-\text{CONR}_2$  (among a formula (R3)) which has one allyl group as a (B) carbon-carbon double bond (meta) acrylamide 99.9 - 80-mol% R1 A hydrogen atom or a methyl group, and R2 The straight chain of a hydrogen atom or carbon numbers 1-4, or the alkyl group of branched chain, R3 the alkyl group of the straight chain of carbon numbers 1-4, or branched chain -- expressing -- additive for paper manufacture which comes to contain the acrylamide system copolymer obtained by copolymerizing 0.05-10-mol % of N-permutation (meta) acrylamides expressed (meta).

[Claim 3] (A) (meta) Acrylamide, the monomer which has one allyl group as a (B) carbon-carbon double bond (meta), (C) General formula (1): $\text{CH}_2=\text{C}(\text{R}_1)-\text{CONR}_2$  (among a formula (R3)) R1 A hydrogen atom or a methyl group, and R2 The straight chain of a hydrogen atom or carbon numbers 1-4, or the alkyl group of branched chain, R3 the alkyl group of the straight chain of carbon numbers 1-4, or branched chain -- expressing -- N-permutation (meta) acrylamides expressed and the anionic vinyl monomer except a (D) (aforementioned A) - (C) component -- The additive for paper manufacture which comes to contain the acrylamide system copolymer obtained by copolymerizing at least one sort chosen from a cationic vinyl monomer and the Nonion nature vinyl monomer (meta).

[Claim 4] (A) (meta) Monomer 0.05 - ten-mol % and (C) general formula (1): $\text{CH}_2=\text{C}(\text{R}_1)-\text{CONR}_2$  (among a formula (R3)) which has one allyl group as a (B) carbon-carbon double bond (meta) acrylamide 99.9 - 55-mol% R1 A hydrogen atom or a methyl group, and R2 The straight chain of a hydrogen atom or carbon numbers 1-4, or the alkyl group of branched chain, R3 the alkyl group of the straight chain of carbon numbers 1-4, or branched chain -- expressing -- the anionic vinyl monomer except 0.05-10-mol % of N-permutation (meta) acrylamides expressed, and a (D) (aforementioned A) - (C) component -- The additive for paper manufacture which comes to contain the acrylamide system copolymer which is chosen from a cationic vinyl monomer and the Nonion nature vinyl monomer, and which is obtained by copolymerizing less than [ 1 sort 40 mol % ] at least (meta).

[Claim 5] (B) The additive for paper manufacture according to claim 1 to 4 whose monomer which has one allyl group as a carbon-carbon double bond (meta) is at least one sort chosen from an allyl compound (meta) carboxylic acid, allyl compound (meta) sulfonic acids, these salts, and (meta) allyl alcohol.

[Claim 6] (C) The additive for paper manufacture according to claim 1 to 4 whose N-permutation (meta) acrylamides are at least one sort chosen from N and N-dimethyl (meta) acrylamide, N-methyl (meta) acrylamide, N-ethyl (meta) acrylamide, N-isopropyl (meta) acrylamide, and N-t-

butyl (meta) acrylamide.

[Claim 7] (D) as a component -- the total mol sum of all monomers -- receiving -- an anionic vinyl monomer -- a 1-15-mol % and cationic vinyl monomer -- 1-15-mol % -- the additive for paper manufacture according to claim 3 or 4 which it comes to use.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the additive for paper manufacture. In detail, it is related with the additive for paper manufacture which comes to contain the acrylamide (meta) system copolymer of high branching structure.

[0002]

[Description of the Prior Art] In recent years, on the occasion of manufacture of paper and the paper board, importance has been attached to the additive for paper manufacture, especially the paper reinforcing agent. It is further raised with the purpose of energy saving or saving resources that use of good pulp was restricted with aggravation of a bolt supply situation as this background and that the need for reuse of used paper became strong much more, and the additive for paper manufacture as a modifier of paper and the paper board is much more indispensable as that result.

[0003] On the other hand, the dependence and its use range of a filtration improvement agent and a paper reinforcing agent have spread further for the purpose of upgrading according to the improvement in the productivity accompanying improvement in the speed of a paper machine, or diversification of paper. As an additive for paper manufacture, a polyacrylamide system is in use under this situation.

[0004] however, conventionally well-known in recent years, since the service condition of the additive for paper manufacture is becoming still severer -- it is coming to the limitation by the additive for polyacrylamide system paper manufacture of low molecular weight in respect of the effectiveness as an additive comparatively. Therefore, the means of macromolecule quantification is taken in order to aim at improvement in the engine performance, but since the viscosity of the copolymer obtained rises too much when macromolecule quantification is only carried out, the dispersibility at the time of paper making serves as a defect. Consequently, when this copolymer is used as an additive for paper manufacture, too much condensation arises, and it is easy to cause the conditions turbulence of perfect paper. Moreover, the high-concentration product (additive for paper manufacture) is demanded from reduction of transportation cost, and the field of improvement in productivity.

[0005] That these troubles should be canceled, branching structure is given by using a cross-linking vinyl monomer (what has at least two double bonds), and the attempt to which you are going to make it increase the molecular weight is made, suppressing a viscosity rise of the copolymer obtained. For example, Uono and others (JP,53-114911,A) has proposed using divinyl system monomers, such as methylenebis acrylamide, as a cross linking agent component. However, Uono and others has also pointed out gelling, if the addition of a divinyl system monomer is increased to coincidence. This is in agreement with the theory (Principles of Polymer Science, Cornell University Press Ithaca N.Y., 1953) of gelation by the system which added the divinyl system monomer which Flory pointed out. Moreover, although Kimura and others recommended 3 organic-functions vinyl monomer (JP,2-61197,A), according to recognition of this invention person or the experiment fact, the gelation effectiveness same as the above is only amplified, and it resulted in making manufacture of the additive for paper

manufacture more difficult compared with the case where a divinyl system monomer is used on the contrary. Moreover, when little use of the cross linking agent was carried out, the polymer of the amount of macromolecules could not be obtained, and the effectiveness as an additive for paper manufacture was not yet enough.

[0006] Moreover, the attempt which is going to give branching structure is also made by using the vinyl monomer which has chain transfer nature substituents, such as allyl compound (meta) acrylate and N,N-dimethylacrylamide, (JP,5-195485,A). However, when the vinyl monomer which has a chain transfer nature substituent is used, although gelation cannot take place easily, molecular weight distribution cannot become large and it cannot obtain the acrylamide (meta) system copolymer of the amount of macromolecules. This is pointed out by said Flory.

[0007]

[Problem(s) to be Solved by the Invention] Without being accompanied by gelation, this invention comes to contain the acrylamide (meta) system copolymer which carried out macromolecule quantification, and also in high concentration, handling nature is comparatively good at hypoviscosity, and it aims at offering the additive for paper manufacture which is moreover excellent in the engine performance as an additive for paper manufacture.

[0008]

[Means for Solving the Problem] As a result of repeating research wholeheartedly that the technical problem of said conventional technique should be solved, this invention persons as a constituent of an acrylamide (meta) system copolymer By using N-permutation (meta) acrylamides expressed with the monomer which has one allyl group as a (B) carbon-carbon double bond (meta) shown below as a monomer which has chain transfer nature, and the (C) general formula (1) It found out that an acrylamide (meta) system copolymer could be comparatively obtained by hypoviscosity by the amount of macromolecules, and high concentration, without being accompanied by gelation. This invention is completed based on the starting new knowledge.

[0009] That is, this invention is monomer and (C) general formula (1):  $\text{CH}_2 = \text{C}(\text{R}_1) - \text{CONR}_2$  (among a formula (R3)) which has one allyl group as a (A) (meta) acrylamide and (B) carbon-carbon double bond (meta). R1 A hydrogen atom or a methyl group, and R2 The straight chain of a hydrogen atom or carbon numbers 1-4, or the alkyl group of branched chain, R3 the alkyl group of the straight chain of carbon numbers 1-4, or branched chain -- expressing -- the additive for paper manufacture which comes to contain the acrylamide system copolymer obtained by copolymerizing N-permutation (meta) acrylamides expressed (meta) -- The monomer in which this invention furthermore has one allyl group as a (A) (meta) acrylamide and (B) carbon-carbon double bond (meta), (C) General formula (1):  $\text{CH}_2 = \text{C}(\text{R}_1) - \text{CONR}_2$  (among a formula (R3)) R1 A hydrogen atom or a methyl group, and R2 The straight chain of a hydrogen atom or carbon numbers 1-4, or the alkyl group of branched chain, R3 the alkyl group of the straight chain of carbon numbers 1-4, or branched chain -- expressing -- N-permutation (meta) acrylamides expressed and the anionic vinyl monomer except a (D) (aforementioned A) - (C) component -- It is related with the additive for paper manufacture which comes to contain the acrylamide system copolymer obtained by copolymerizing at least one sort chosen from a cationic vinyl monomer and the Nonion nature vinyl monomer (meta).

[0010]

[Embodiment of the Invention] In this invention, (A) (meta) acrylamide means acrylamide or methacrylamide, it can be independent-used or these can be used together. It is good to carry out independent use of the acrylamide from the field of economical efficiency. in addition, following this invention -- setting (meta) -- it is the same semantics.

[0011] (B) The monomer which has one allyl group as a carbon-carbon double bond (meta) means the monomer which has one allyl group (meta) in a molecule, and does not have a carbon-carbon double bond other than an allyl group (meta). (Meta) An allyl group is a functional group which generally has chain transfer nature, and it is thought in this invention that it has the function of both a chain transfer agent and a cross linking agent. In addition, since two or more allyl groups (meta) gel in a certain case or molecular weight distribution become large into a molecule, it is not desirable. Moreover, the same is said of the case where it has other different

carbon-carbon double bonds from an allyl group (meta), for example, an acryloyl radical etc. As a monomer which has one allyl group as such a (B) carbon-carbon double bond (meta), at least one sort chosen from an allyl compound (meta) sulfonic acid, allyl compound (meta) carboxylic acids, these salts, and (meta) allyl alcohol can be used. Also in these (B) components, an allyl compound (meta) sulfonic acid or its salt is desirable at the point in which the acrylamide system copolymer obtained (meta) carries out macromolecule quantification, and a meta-allyl compound sulfonic acid or its salt is more desirable from the stability of a monomer especially. In addition, as a salt, alkali-metal salts, such as sodium salt and potassium salt, ammonium salt, etc. are raised.

[0012] (C) general formula (1):  $\text{CH}_2=\text{C}(\text{R}_1)-\text{CONR}_2$  ( $\text{R}(\text{R}_3)$  1 -- a hydrogen atom or a methyl group --)  $\text{R}_2$  The straight chain of a hydrogen atom or carbon numbers 1-4, or the alkyl group of branched chain,  $\text{R}_3$  N-permutation (meta) acrylamides expressed with the alkyl group of the straight chain of carbon numbers 1-4 or branched chain It is going to introduce much branching structure into the copolymer obtained by this using the methyl group or methylene group in N-alkyl group acting as a chain transfer point. If this technique is used, branched polymer without gelation can be obtained.  $\text{R}_2$  in said general formula (1) Or  $\text{R}_3$  With the alkyl group of the straight chain of carbon numbers 1-4 which can be set, or branched chain, a methyl group, an ethyl group, an isopropyl group, t-butyl, etc. are raised. (C) As an example of a component, N and N-dimethyl (meta) acrylamide, N-isopropyl (meta) acrylamide, N-methyl (meta) acrylamide, N-ethyl (meta) acrylamide, N-isopropyl (meta) acrylamide, and N-t-butyl (meta) acrylamide are raised, and at least one sort chosen from these can be used. Dimethyl acrylamide is desirable in respect of copolymeric and chain transfer nature also in these (C) components.

[0013] Although it contributes to the branching reaction by chain transfer, molecular weight distribution cannot become large and, as for the aforementioned (C) component, cannot fully raise molecular weight only of the (C) component. This invention can acquire the acrylamide (meta) system copolymer of the amount of macromolecules with narrow molecular weight distribution by combining said specific (B) component which acts also as a cross linking agent and has the chain transfer effectiveness in addition to the (C) component which carries out a branching reaction. Therefore, it replaces with the (B) component, and even if it combines with the (C) component chain transfer agents generally known, such as isopropyl alcohol, the molecular weight distribution of this invention cannot acquire the acrylamide (meta) system copolymer of the narrow amount of macromolecules. In addition, when it replaces with the (C) component and the conventional cross-linking vinyl monomer (what has at least two double bonds) is used, as mentioned above (meta), it is easy to gel an acrylamide system copolymer, and manufacture of the additive for paper manufacture in high concentration is difficult.

[0014] this invention -- as the constituent of an acrylamide (meta) system copolymer -- the aforementioned (A) component, the (B) component, and the (C) component -- in addition, at least one sort chosen from the anionic vinyl monomer except the -- (C) component (aforementioned [A]), a cationic vinyl monomer, and the Nonion nature vinyl monomer as a (D) component can be used further. Namely, what is necessary is just to use a cationic vinyl monomer, in what is necessary's being just to use an anionic vinyl monomer in giving anionic to the copolymer obtained and giving cationicity to the copolymer obtained. What is necessary is just to use both anionic vinyl monomer and cationic vinyl monomer, in giving anionic and cationicity to the copolymer obtained and making it both sexes. Moreover, it is used in order to give hydrophobicity to a polymer, and it can use together with the -- (C) component (aforementioned [A]) independently, and also the Nonion nature vinyl monomer can also be used together combining said ionicity vinyl monomer.

[0015] As an anionic vinyl monomer in the aforementioned (D) component, alkali-metal salts, such as sodium salt of organic sulfonic-acids [such as dicarboxylic acid; vinyl sulfonic acids, such as monocarboxylic acid; maleic acids, such as an acrylic acid and a crotonic acid, boletic acid, an itaconic acid, and muconic acid, a styrene sulfonic acid, and 2-acrylamido-2-methyl propane sulfonic acid]; or these various organic acids and potassium salt, ammonium salt, etc. are raised, for example (meta).

[0016] (D) As a cationic vinyl monomer in a component For example, dimethylaminoethyl (meta)

acrylate, diethylaminoethyl (meta) acrylate, The vinyl monomers which have the third class amino groups, such as dimethylaminopropyl (meta) acrylamide and diethylamino propyl (meta) acrylamide, or those hydrochloric acids, The salts of inorganic acids, such as a sulfuric acid and an acetic acid, or an organic acid, or this the third class amino-group content vinyl monomer and methyl chloride, The vinyl monomer containing the quaternary ammonium salt obtained by the reaction with the fourth class-ized agents, such as benzyl chloride, a dimethyl sulfate, and epichlorohydrin, etc. is raised.

[0017] (D) As an Nonion nature vinyl monomer in a component, the alkyl ester (carbon numbers 1-8 of an alkyl group) of said anionic vinyl monomer, acrylonitrile, styrene, vinyl acetate, the methyl vinyl ether, etc. are raised. In addition, little use of the conventional cross-linking vinyl monomer can also be carried out within limits which do not deviate from the engine performance of the additive for paper manufacture of this invention.

[0018] In this invention, the amount of each [ used ] of each component of the copolymer which consists of a (A) - (C) component must be determined enough in consideration of the engine performance as an additive for paper manufacture of the copolymer obtained. namely, the (A) component -- the total mol sum of (A) - (C) component -- receiving -- usually -- about 99.9-80 mol % -- desirable -- 99.2 - 80-mol % -- it is 99.2 - 90-mol % more preferably. the case where the (D) component is used on the other hand -- the (A) component -- the total mol sum of (A) - (D) component -- receiving -- usually -- about 99.9-55 mol % -- it is 99.2 - 70-mol % preferably. In addition, when not filling the (A) component to 55-mol%, it is difficult to get in sufficient paper durability effectiveness as an additive for paper manufacture etc.

[0019] (B) a component -- the same -- the total mol sum of (A) - (C) component, or the total mol sum of (A) - (D) component -- receiving -- usually -- 0.05 - ten-mol % -- it is 0.1 - five-mol % preferably. (B) Since the effectiveness of chain transfer is small and generation of the branch point also has it when not filling a component to 0.05-mol%, branching structure is inadequate. [ little ] Since the effectiveness of chain transfer is too strong when exceeding ten-mol %, a polymer chain becomes short and it is hard coming to generate the amount polymer of macromolecules.

[0020] (C) a component -- the same -- said total mol sum -- receiving -- usually -- 0.05-10-mol % -- it is 0.1-5-mol % preferably. (C) Since there is little generation of the branch point when not filling a component to 0.05-mol%, branching structure is inadequate. In exceeding ten-mol %, there is an inclination for the branching reaction by chain transfer to increase and to cause gelation.

[0021] moreover -- the case where the (D) component is used -- the total mol sum of (A) - (D) component -- receiving -- usually -- or less about 40 mol % -- it is used less than [ 30 mol % ] preferably. (D) When a component exceeds 40-mol %, it is difficult to get in sufficient paper durability effectiveness. in addition -- the case where anionic is given to a copolymer as a (D) component -- said total mol sum -- receiving -- usually -- an anionic vinyl monomer -- 1 - 20-mol % -- desirable -- 2 - 15-mol % -- it is used. the case where cationicity is given to a copolymer -- the total mol sum -- receiving -- usually -- a cationic vinyl monomer -- 1-20-mol % -- desirable -- 2-15-mol % -- it is used. moreover -- the case where both sexes are given to a copolymer -- the total mol sum -- receiving -- usually -- an anionic vinyl monomer -- 1-15-mol % -- desirable -- a 2-10-mol % and cationic vinyl monomer -- 1-15-mol % -- desirable -- 2-10-mol % -- it is used.

[0022] Composition of the copolymer used for this invention can be conventionally performed by various well-known approaches. For example, said various monomers ((A) - (C) component or (A) - (D) component) and water can be taught to a predetermined reaction container, a radical polymerization initiator can be added, and the water-soluble acrylamide (meta) system copolymer made into the purpose by warming under churning can be obtained. Reaction temperature is about 50-100 degrees C, and reaction time is usually about 1 - 5 hours. Reaction concentration (monomer concentration) can usually be performed at about 10 - 40 % of the weight, and can carry out a polymerization also in high concentration. Moreover, without diluting also in a high-concentration case, it can be used and the water solution of the obtained copolymer can be saved. In addition, an approach to teach a monomer can be performed by the various approaches



that a coincidence polymerization, a continuation dropping polymerization, etc. are conventionally well-known. As a radical polymerization initiator, the usual radical polymerization initiators, such as a redox system polymerization initiator of the form which combined persulfate, such as potassium persulfate and ammonium persulfate, or these and the reducing agent like a sodium hydrogensulfite, can be used. Moreover, an azo system initiator may be used together to said radical polymerization initiator. the amount of the radical polymerization initiator used -- 0.05- of the AUW sum of a monomer -- it is 0.1 - 0.5 % of the weight preferably 2.0% of the weight. At 0.05 % of the weight, when the polymerization itself does not fully advance but it crosses 2.0 % of the weight of another side, it is difficult to obtain the amount polymer of macromolecules.

[0023] Weight average molecular weight is 500,000 to about 6 million, and can usually use the acrylamide (meta) system copolymer obtained in this way as various kinds of additives for paper manufacture, such as a layer indirect arrival agent of \*\*\*\*\* and \*\*\*\* doubling paper, outside internal chemicals, such as a filtration improvement agent and a paper reinforcing agent, a surface paper reinforcing agent, etc. In addition, when using as a layer indirect arrival agent of internal chemicals, such as a filtration improvement agent and a paper reinforcing agent, and \*\*\*\* doubling paper etc., it is desirable that weight average molecular weight is 2 million or more. Moreover, viscosity is good to usually use about (25 degrees C) 10000cps by the following descriptions from the point of handling nature. In addition, although the additive for paper manufacture of this invention is adjusted to 10 - 40 % of the weight of solid content concentration, it can adjust about (25 degrees C) 10000cps of viscosity for solid content concentration to 40% of the weight of a case below. Thus, although the additive for paper manufacture which comes to contain the acrylamide (meta) system copolymer of this invention is the amount of macromolecules, it is hypoviscosity and can be used by high solid content concentration.

[0024]

[Effect of the Invention] Although the additive for paper manufacture of this invention contains the acrylamide (meta) system copolymer of the amount of (1) macromolecules, it is hypoviscosity comparatively and excellent also in workability. Moreover, transportation cost is sharply reducible, while high-concentration-izing of product concentration is possible and being able to improve productivity. Moreover, it can guess that the acrylamide system copolymer (2) Obtained (meta) is high branching structure, and the contact between pulp fiber shows many various characteristic engine performance as additives for paper manufacture, such as a paper durability enhancing effect. Many effectiveness which was excellent also in the bottom of the latest severe paper-making conditions as the result as various kinds of additives for paper manufacture, such as a layer indirect arrival agent of \*\*\*\*\* and \*\*\*\* doubling paper, outside internal chemicals, such as a filtration improvement agent and a paper reinforcing agent, a surface paper reinforcing agent, etc. is done so.

[0025]

[Example] Hereafter, an example and the example of a comparison are given and this invention is explained more concretely. In addition, each of sections and %s is based on weight criteria, as long as there is no special mention.

[0026] The acrylamide 234.6 section (it is the same as that below of 95 below [ % and ] to the total mol sum of a monomer), the meta-allyl compound sulfonic-acid soda 16.5 section (three-mol %), the dimethyl acrylamide 6.9 section (two-mol %), and the ion-exchange-water 960 section (21% of monomer concentration) were taught to the 4 opening flask equipped with example 1 agitator, a thermometer, a reflux cooling pipe, and nitrogen gas installation tubing, and the oxygen in the system of reaction was removed through nitrogen gas. The inside of a system was made into 40 degrees C, and the ammonium persulfate 0.25 section and the sodium-hydrogensulfite 0.15 section were supplied as a polymerization initiator to the bottom of churning. It was kept warm for 2 hours, after carrying out a temperature up to 90 degrees C. The ion-exchange-water 70 section (it adjusts to 20% of solid content concentration) was supplied after polymerization termination, pH4.5, 20.2% of solid content, and viscosity (25 degrees C) obtained 9800cps, and weight average molecular weight obtained the copolymer water solution of 2,900,000. Moreover, it was 0% when the amount of gels was measured. In addition, although the amount of gels does

not pass this filter when filtering a sample with a 0.45-micrometer membrane filter, it means a content (% of the weight).

[0027] In examples 2-11 and one to example of comparison 5 example 1, as shown in Table 1, even if few [ either ] among the class of (A) - (D) component, or its operating rate, one sort was changed, and also the same actuation as an example 1 was performed, and various copolymer water solutions were obtained. the description of the obtained various copolymer water solutions -- a value is shown in Table 2. In addition, in the example 10, the polymerization was performed at 41% of monomer concentration, and after polymerization termination, ion exchange water was thrown in so that it might become 40% of solid content concentration. Moreover, in the examples 4 and 5 of a comparison, it carried out by adding isopropyl alcohol.

[0028]

[Table 1]

	モノマーの種類および使用割合（モル％）												
	(A) 成分		(B) 成分		(C) 成分		(D) 成分			その他			
							アニオン	カチオン	ノニオン				
実施例 1	AM	95	SMAS	3	DMAA	2	—	—	—				
実施例 2	AM	90	SMAS	3	DMAA	2	AA	5	—	—			
実施例 3	AM	90	SMAS	3	DMAA	2	—	DM	5	—			
実施例 4	AM	89	SMAS	3	DMAA	2	AA	3	DM	3	—		
実施例 5	AM	85	SMAS	3	DMAA	2	—	—	—	AN10			
実施例 6	AM	89	SMAS	3	IPAA	2	AA	3	DM	3	—		
実施例 7	AM	89	SAS	3	DMAA	2	AA	3	DM	3	—		
実施例 8	AM	89	SAS	3	IPAA	2	AA	3	DM	3	—		
実施例 9	AM	87	SAS	5	IPAA	2	AA	3	DM	3	—		
実施例 10	AM	85	SAS	7	IPAA	2	AA	3	DM	3	—		
実施例 11	AM	90	SAS	2	DMAA	2	IA	3	DM	3	—		
比較例 1	AM	90.5	SMAS	3	—	—	AA	3	DM	3	—	AMA	0.5
比較例 2	AM	90.8	SMAS	3	—	—	AA	3	DM	3	—	TAIC	0.2
比較例 3	AM	89	SMAS	3	—	—	AA	3	DM	3	—	N-MAA	2
比較例 4	AM	92	—	—	DMAA	2	AA	3	DM	3	—	IPA	5
比較例 5	AM	92	—	—	DMAA	2	IA	3	DM	3	—	IPA	3

[0029] Front Naka, AM:acrylamide, SMAS:meta-allyl-compound sulfonic-acid soda, SAS:allyl-compound sulfonic-acid soda, DMAA:N,N-dimethylacrylamide, IPAA:N-isopropyl acrylamide, AA:acrylic acid, IA:itaconic acid, DM:dimethylaminoethyl methacrylate, AMA:allyl-compound methacrylate, TAIC:triallyl isocyanurate, N-MAA:N-methoxy acrylamide, IPA: Express isopropyl alcohol.

[0030]

[Table 2]

	性 状				
	pH	固形分 (%)	粘度 (c p s)	重量平均分子量	ゲル量 (%)
実施例 1	4. 5	20. 2	9 8 0 0	$290 \times 10^4$	0
実施例 2	4. 2	20. 5	9 3 0 0	$270 \times 10^4$	0
実施例 3	4. 7	20. 4	8 9 0 0	$325 \times 10^4$	0
実施例 4	4. 5	20. 5	9 5 0 0	$310 \times 10^4$	0
実施例 5	4. 3	20. 8	9 9 0 0	$250 \times 10^4$	0
実施例 6	4. 5	20. 2	9 1 0 0	$275 \times 10^4$	0
実施例 7	4. 4	20. 5	9 3 0 0	$285 \times 10^4$	0
実施例 8	4. 5	20. 8	9 6 0 0	$280 \times 10^4$	0
実施例 9	4. 5	20. 5	9 3 0 0	$280 \times 10^4$	0
実施例 10	4. 5	40. 2	9 5 0 0	$520 \times 10^4$	0
実施例 11	4. 0	20. 5	8 0 0 0	$300 \times 10^4$	0
比較例 1	4. 6	20. 3	9 1 0 0	$220 \times 10^4$	15
比較例 2	4. 5	20. 5	9 5 0 0	$240 \times 10^4$	20
比較例 3	4. 5	20. 2	7 8 0 0	$185 \times 10^4$	0
比較例 4	4. 7	20. 3	7 3 0 0	$170 \times 10^4$	0
比較例 5	4. 2	20. 3	9 0 0 0	$220 \times 10^4$	0

[0031] Beating is carried out with a beater. (The performance-evaluation approach 1) corrugated paper used paper -- a Niagara style -- Add a sulfuric-acid band 1.6% to the pulp adjusted to Canadian standard freeness (C. S.F) 420ml, and it is referred to as pH5.5. Subsequently, 0.6% for pulp is added by making into a paper reinforcing agent each copolymer water solution obtained in examples 1-11 or the examples 1-5 of a comparison. After agitating, pulp slurry concentration is diluted so that it may become 0.1%, and it is basis-weight 150 g/m<sup>2</sup> with the TAPPI sheet machine. Paper making is carried out so that it may become, and it is 2 5kg/cm. Press dehydration was carried out for 2 minutes. after [ subsequently, / JIS ] drying for 3 minutes in 105 degrees C with a rotation mold dryer and carrying out gas conditioning to the bottom of the condition of 20 degrees C and 65%R.H. for 24 hours P 8112 -- applying correspondingly -- a ratio -- bursting strength was measured. A result is shown in Table 3.

[0032] (The performance-evaluation approach 2) N-BKP -- a Niagara style -- each copolymer water solution obtained in each above-mentioned example and the example of a comparison by the pulp (pH6.8) which carried out beating with the beater, and which was adjusted to 550 (C. S.F)ml -- the above -- the same -- adding -- the same actuation as the above -- carrying out -- a ratio -- bursting strength was measured. A result is shown in Table 3.

[0033]

[Table 3]

	評価方法 1	評価方法 2
実施例 1	2. 5 5	5. 8 0
実施例 2	2. 6 0	5. 8 5
実施例 3	2. 6 3	5. 8 9
実施例 4	2. 7 0	5. 9 6
実施例 5	2. 6 4	5. 9 0
実施例 6	2. 6 8	5. 9 3
実施例 7	2. 6 7	5. 9 1
実施例 8	2. 6 8	5. 9 5
実施例 9	2. 6 9	5. 9 6
実施例 10	2. 5 1	5. 7 3
実施例 11	2. 6 3	5. 8 3
比較例 1	2. 4 5	5. 5 8
比較例 2	2. 4 0	5. 5 2
比較例 3	2. 3 7	5. 4 8
比較例 4	2. 3 5	5. 5 0
比較例 5	2. 4 0	5. 4 2

[0034] From the result of Table 3, it is admitted that the additive for paper manufacture using the acrylamide system copolymer obtained by this invention discovers the outstanding paper durability enhancing effect.

[0035] In examples 12-17 and example of comparison 6 example 1, as shown in Table 4, even if few [ either ] among the class of (A) - (D) component, or its operating rate, one sort was changed, and also the same actuation as an example 1 was performed, and various copolymer water solutions were obtained. the description of the obtained various copolymer water solutions -- a value is shown in Table 5. In addition, in each example and the example of a comparison, the polymerization was performed at 21% of monomer concentration, 31%, or 41%, and ion exchange water was thrown in after polymerization termination, and it prepared so that it might become the solid content concentration (20%, 30%, or about 40%) shown in Table 5.

[0036]

[Table 4]

	モノマーの種類および使用割合 (モル%)						
	(A) 成分	(B) 成分	(C) 成分	(D) 成分			その他
				アニオン	カチオン	ノニオン	
実施例12	AM 93.5	SMAS 0.5	DMAA 1	IA 5	---	---	
実施例13	AM 68	SMAS 1	DMAA 1	AA 5	---	AN25	
実施例14	AM 93	SMAS 2	DMAA 1	---	DM 5	---	
実施例15	AM 83	SMAS 1	DMAA 1	IA 5	---	AN10	
実施例16	AM 87	SMAS 2	DMAA 1	IA10	---	---	
実施例17	AM 62	SMAS 2	DMAA 1	AA 5	---	AN30	
比較例 6	AM 68.5	SMAS 1	----	AA 5		AN25	AMA 0.5

[0037] Front Naka, AM:acrylamide, SMAS:meta-allyl-compound sulfonic-acid soda, DMAA:N,N-dimethylacrylamide, IA:itaconic acid, AA:acrylic acid, DM:dimethylaminoethyl methacrylate, AN:acrylonitrile, AMA: Express allyl compound methacrylate.

[0038]

[Table 5]

	性 状				
	pH	固形分 (%)	粘度 (c p s)	重量平均分子量	ゲル量 (%)
実施例12	5. 5	30. 8	8500	$131 \times 10^4$	0
実施例13	5. 3	30. 0	9200	$100 \times 10^4$	0
実施例14	4. 7	20. 5	9900	$182 \times 10^4$	0
実施例15	5. 1	30. 7	4700	$156 \times 10^4$	0
実施例16	5. 3	40. 2	9300	$122 \times 10^4$	0
実施例17	5. 2	40. 4	4100	$93 \times 10^4$	0
比較例 6	5. 5	30. 0	12000	$170 \times 10^4$	15

[0039] (The performance-evaluation approach 3) Lab size press coating equipment (Kumagai Riki Kogyo make) was used for high-quality acid paper (basis-weight 60 g/m<sup>2</sup>), and after it carried out coating (a part for 40m/in 2% of coating concentration, nip pressure 15 kg/cm, and coating rate), having used as the paper reinforcing agent each copolymer water solution obtained in examples 10-16 or the examples 5-6 of a comparison, it dried for 1 minute at 105 degrees C using the rotation dryer. After desiccation, after carrying out gas conditioning to the bottom of the condition of 20 degrees C and 65%R.H. for 24 hours, RI printing testing machine (product made from \*\*\*\*\*) performed the surface strength test using the nip pressure of 4mm, and SMX ink (the TOYO INK MFG. CO., LTD. make, tuck 20), and the picking condition after printing was observed with the naked eye. 5 was made into good and it considered as five-step evaluation by making 1 into wrong. A result is shown in Table 6.

[0040] (The performance-evaluation approach 4) It is J.TAPPI about the interior reinforcement (Kgf-cm) after carrying out gas conditioning like the performance-evaluation approach 3. It

measured according to No.54. A result is shown in Table 6.

[0041]

[Table 6]

	評価方法 3	評価方法 4
実施例12	4. 9	2. 5 6
実施例13	4. 4	2. 5 3
実施例14	4. 7	2. 5 5
実施例15	4. 7	2. 5 5
実施例16	4. 9	2. 5 4
実施例17	4. 4	2. 5 5
比較例 6	4. 1	2. 4 5

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TECHNICAL FIELD

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[Field of the Invention] This invention relates to the additive for paper manufacture. In detail, it is related with the additive for paper manufacture which comes to contain the acrylamide (meta) system copolymer of high branching structure.

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PRIOR ART

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[Description of the Prior Art] In recent years, on the occasion of manufacture of paper and the paper board, importance has been attached to the additive for paper manufacture, especially the paper reinforcing agent. It is further raised with the purpose of energy saving or saving resources that use of good pulp was restricted with aggravation of a bolt supply situation as this background and that the need for reuse of used paper became strong much more, and the additive for paper manufacture as a modifier of paper and the paper board is much more indispensable as that result.

[0003] On the other hand, the dependence and its use range of a filtration improvement agent and a paper reinforcing agent have spread further for the purpose of upgrading according to the improvement in the productivity accompanying improvement in the speed of a paper machine, or diversification of paper. As an additive for paper manufacture, a polyacrylamide system is in use under this situation.

[0004] however, conventionally well-known in recent years, since the service condition of the additive for paper manufacture is becoming still severer -- it is coming to the limitation by the additive for polyacrylamide system paper manufacture of low molecular weight in respect of the effectiveness as an additive comparatively. Therefore, the means of macromolecule quantification is taken in order to aim at improvement in the engine performance, but since the viscosity of the copolymer obtained rises too much when macromolecule quantification is only carried out, the dispersibility at the time of paper making serves as a defect. Consequently, when this copolymer is used as an additive for paper manufacture, too much condensation arises, and it is easy to cause the conditions turbulence of perfect paper. Moreover, the high-concentration product (additive for paper manufacture) is demanded from reduction of transportation cost, and the field of improvement in productivity.

[0005] That these troubles should be canceled, branching structure is given by using a cross-linking vinyl monomer (what has at least two double bonds), and the attempt to which you are going to make it increase the molecular weight is made, suppressing a viscosity rise of the copolymer obtained. For example, Uono and others (JP,53-114911,A) has proposed using divinyl system monomers, such as methylenebis acrylamide, as a cross linking agent component. However, Uono and others has also pointed out gelling, if the addition of a divinyl system monomer is increased to coincidence. This is in agreement with the theory (Principles of Polymer Science, Cornell University Press Ithaca N.Y., 1953) of gelation by the system which added the divinyl system monomer which Flory pointed out. Moreover, although Kimura and others recommended 3 organic-functions vinyl monomer (JP,2-61197,A), according to recognition of this invention person or the experiment fact, the gelation effectiveness same as the above is only amplified, and it resulted in making manufacture of the additive for paper manufacture more difficult compared with the case where a divinyl system monomer is used on the contrary. Moreover, when little use of the cross linking agent was carried out, the polymer of the amount of macromolecules could not be obtained, and the effectiveness as an additive for paper manufacture was not yet enough.

[0006] Moreover, the attempt which is going to give branching structure is also made by using the vinyl monomer which has chain transfer nature substituents, such as allyl compound (meta)



acrylate and N,N-dimethylacrylamide, (JP,5-195485,A). However, when the vinyl monomer which has a chain transfer nature substituent is used, although gelation cannot take place easily, molecular weight distribution cannot become large and it cannot obtain the acrylamide (meta) system copolymer of the amount of macromolecules. This is pointed out by said Flory.

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EFFECT OF THE INVENTION

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[Effect of the Invention] Although the additive for paper manufacture of this invention contains the acrylamide (meta) system copolymer of the amount of (1) macromolecules, it is hypoviscosity comparatively and excellent also in workability. Moreover, transportation cost is sharply reducible, while high-concentration-izing of product concentration is possible and being able to improve productivity. Moreover, it can guess that the acrylamide system copolymer (2) Obtained (meta) is high branching structure, and the contact between pulp fiber shows many various characteristic engine performance as additives for paper manufacture, such as a paper durability enhancing effect. Many effectiveness which was excellent also in the bottom of the latest severe paper-making conditions as the result as various kinds of additives for paper manufacture, such as a layer indirect arrival agent of \*\*\*\*\* and \*\*\*\* doubling paper, outside internal chemicals, such as a filtration improvement agent and a paper reinforcing agent, a surface paper reinforcing agent, etc. is done so.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] Without being accompanied by gelation, this invention comes to contain the acrylamide (meta) system copolymer which carried out macromolecule quantification, and also in high concentration, handling nature is comparatively good at hypoviscosity, and it aims at offering the additive for paper manufacture which is moreover excellent in the engine performance as an additive for paper manufacture.

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MEANS

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[Means for Solving the Problem] As a result of repeating research wholeheartedly that the technical problem of said conventional technique should be solved, this invention persons as a constituent of an acrylamide (meta) system copolymer By using N-permutation (meta) acrylamides expressed with the monomer which has one allyl group as a (B) carbon-carbon double bond (meta) shown below as a monomer which has chain transfer nature, and the (C) general formula (1) It found out that an acrylamide (meta) system copolymer could be comparatively obtained by hypoviscosity by the amount of macromolecules, and high concentration, without being accompanied by gelation. This invention is completed based on the starting new knowledge.

[0009] That is, this invention is monomer and (C) general formula (1):  $\text{CH}_2 = \text{C}(\text{R}_1) - \text{CONR}_2$  (among a formula (R3)) which has one allyl group as a (A) (meta) acrylamide and (B) carbon-carbon double bond (meta). R1 A hydrogen atom or a methyl group, and R2 The straight chain of a hydrogen atom or carbon numbers 1-4, or the alkyl group of branched chain, R3 the alkyl group of the straight chain of carbon numbers 1-4, or branched chain -- expressing -- the additive for paper manufacture which comes to contain the acrylamide system copolymer obtained by copolymerizing N-permutation (meta) acrylamides expressed (meta) -- The monomer in which this invention furthermore has one allyl group as a (A) (meta) acrylamide and (B) carbon-carbon double bond (meta), (C) General formula (1):  $\text{CH}_2 = \text{C}(\text{R}_1) - \text{CONR}_2$  (among a formula (R3)) R1 A hydrogen atom or a methyl group, and R2 The straight chain of a hydrogen atom or carbon numbers 1-4, or the alkyl group of branched chain, R3 the alkyl group of the straight chain of carbon numbers 1-4, or branched chain -- expressing -- N-permutation (meta) acrylamides expressed and the anionic vinyl monomer except a (D) (aforementioned A) - (C) component -- It is related with the additive for paper manufacture which comes to contain the acrylamide system copolymer obtained by copolymerizing at least one sort chosen from a cationic vinyl monomer and the Nonion nature vinyl monomer (meta).

[0010]

[Embodiment of the Invention] In this invention, (A) (meta) acrylamide means acrylamide or methacrylamide, it can be independent-used or these can be used together. It is good to carry out independent use of the acrylamide from the field of economical efficiency. in addition, following this invention -- setting (meta) -- it is the same semantics.

[0011] (B) The monomer which has one allyl group as a carbon-carbon double bond (meta) means the monomer which has one allyl group (meta) in a molecule, and does not have a carbon-carbon double bond other than an allyl group (meta). (Meta) An allyl group is a functional group which generally has chain transfer nature, and it is thought in this invention that it has the function of both a chain transfer agent and a cross linking agent. In addition, since two or more allyl groups (meta) gel in a certain case or molecular weight distribution become large into a molecule, it is not desirable. Moreover, the same is said of the case where it has other different carbon-carbon double bonds from an allyl group (meta), for example, an acryloyl radical etc. As a monomer which has one allyl group as such a (B) carbon-carbon double bond (meta), at least one sort chosen from an allyl compound (meta) sulfonic acid, allyl compound (meta) carboxylic acids, these salts, and (meta) allyl alcohol can be used. Also in these (B) components, an allyl

compound (meta) sulfonic acid or its salt is desirable at the point in which the acrylamide system copolymer obtained (meta) carries out macromolecule quantification, and a meta-allyl compound sulfonic acid or its salt is more desirable from the stability of a monomer especially. In addition, as a salt, alkali-metal salts, such as sodium salt and potassium salt, ammonium salt, etc. are raised.

[0012] (C) general formula (1):  $\text{CH}_2=\text{C}(\text{R}_1)-\text{CONR}_2$  ( $\text{R}(\text{R}_3)$  1 -- a hydrogen atom or a methyl group --)  $\text{R}_2$  The straight chain of a hydrogen atom or carbon numbers 1-4, or the alkyl group of branched chain,  $\text{R}_3$  N-permutation (meta) acrylamides expressed with the alkyl group of the straight chain of carbon numbers 1-4 or branched chain. It is going to introduce much branching structure into the copolymer obtained by this using the methyl group or methylene group in N-alkyl group acting as a chain transfer point. If this technique is used, branched polymer without gelation can be obtained.  $\text{R}_2$  in said general formula (1) Or  $\text{R}_3$  With the alkyl group of the straight chain of carbon numbers 1-4 which can be set, or branched chain, a methyl group, an ethyl group, an isopropyl group, t-butyl, etc. are raised. (C) As an example of a component, N and N-dimethyl (meta) acrylamide, N-isopropyl (meta) acrylamide, N-methyl (meta) acrylamide, N-ethyl (meta) acrylamide, N-isopropyl (meta) acrylamide, and N-t-butyl (meta) acrylamide are raised, and at least one sort chosen from these can be used. Dimethyl acrylamide is desirable in respect of copolymeric and chain transfer nature also in these (C) components.

[0013] Although it contributes to the branching reaction by chain transfer, molecular weight distribution cannot become large and, as for the aforementioned (C) component, cannot fully raise molecular weight only of the (C) component. This invention can acquire the acrylamide (meta) system copolymer of the amount of macromolecules with narrow molecular weight distribution by combining said specific (B) component which acts also as a cross linking agent and has the chain transfer effectiveness in addition to the (C) component which carries out a branching reaction. Therefore, it replaces with the (B) component, and even if it combines with the (C) component chain transfer agents generally known, such as isopropyl alcohol, the molecular weight distribution of this invention cannot acquire the acrylamide (meta) system copolymer of the narrow amount of macromolecules. In addition, when it replaces with the (C) component and the conventional cross-linking vinyl monomer (what has at least two double bonds) is used, as mentioned above (meta), it is easy to gel an acrylamide system copolymer, and manufacture of the additive for paper manufacture in high concentration is difficult.

[0014] this invention -- as the constituent of an acrylamide (meta) system copolymer -- the aforementioned (A) component, the (B) component, and the (C) component -- in addition, at least one sort chosen from the anionic vinyl monomer except the -- (C) component (aforementioned [ A ]), a cationic vinyl monomer, and the Nonion nature vinyl monomer as a (D) component can be used further. Namely, what is necessary is just to use a cationic vinyl monomer, in what is necessary's being just to use an anionic vinyl monomer in giving anionic to the copolymer obtained and giving cationicity to the copolymer obtained. What is necessary is just to use both anionic vinyl monomer and cationic vinyl monomer, in giving anionic and cationicity to the copolymer obtained and making it both sexes. Moreover, it is used in order to give hydrophobicity to a polymer, and it can use together with the -- (C) component (aforementioned [ A ]) independently, and also the Nonion nature vinyl monomer can also be used together combining said ionicity vinyl monomer.

[0015] As an anionic vinyl monomer in the aforementioned (D) component, alkali-metal salts, such as sodium salt of organic sulfonic-acids [ , such as dicarboxylic acid; vinyl sulfonic acids, such as monocarboxylic acid; maleic acids, such as an acrylic acid and a crotonic acid, boletic acid, an itaconic acid, and muconic acid, a styrene sulfonic acid, and 2-acrylamido-2-methyl propane sulfonic acid ]; or these various organic acids and potassium salt, ammonium salt, etc. are raised, for example (meta).

[0016] (D) As a cationic vinyl monomer in a component For example, dimethylaminoethyl (meta) acrylate, diethylaminoethyl (meta) acrylate, The vinyl monomers which have the third class amino groups, such as dimethylaminopropyl (meta) acrylamide and diethylamino propyl (meta) acrylamide, or those hydrochloric acids, The salts of inorganic acids, such as a sulfuric acid and an acetic acid, or an organic acid, or this the third class amino-group content vinyl monomer and

methyl chloride, The vinyl monomer containing the quarternary ammonium salt obtained by the reaction with the fourth class-ized agents, such as benzyl chloride, a dimethyl sulfate, and epichlorohydrin, etc. is raised.

[0017] (D) As an Nonion nature vinyl monomer in a component, the alkyl ester (carbon numbers 1-8 of an alkyl group) of said anionic vinyl monomer, acrylonitrile, styrene, vinyl acetate, the methyl vinyl ether, etc. are raised. In addition, little use of the conventional cross-linking vinyl monomer can also be carried out within limits which do not deviate from the engine performance of the additive for paper manufacture of this invention.

[0018] In this invention, the amount of each [ used ] of each component of the copolymer which consists of a (A) - (C) component must be determined enough in consideration of the engine performance as an additive for paper manufacture of the copolymer obtained. namely, the (A) component -- the total mol sum of (A) - (C) component -- receiving -- usually -- about 99.9-80 mol % -- desirable -- 99.2 - 80-mol % -- it is 99.2 - 90-mol % more preferably. the case where the (D) component is used on the other hand -- the (A) component -- the total mol sum of (A) - (D) component -- receiving -- usually -- about 99.9-55 mol % -- it is 99.2 - 70-mol % preferably. In addition, when not filling the (A) component to 55-mol%, it is difficult to get in sufficient paper durability effectiveness as an additive for paper manufacture etc.

[0019] (B) a component -- the same -- the total mol sum of (A) - (C) component, or the total mol sum of (A) - (D) component -- receiving -- usually -- 0.05 - ten-mol % -- it is 0.1 - five-mol % preferably. (B) Since the effectiveness of chain transfer is small and generation of the branch point also has it when not filling a component to 0.05-mol%, branching structure is inadequate. [ little ] Since the effectiveness of chain transfer is too strong when exceeding ten-mol %, a polymer chain becomes short and it is hard coming to generate the amount polymer of macromolecules.

[0020] (C) a component -- the same -- said total mol sum -- receiving -- usually -- 0.05-10-mol % -- it is 0.1-5-mol % preferably. (C) Since there is little generation of the branch point when not filling a component to 0.05-mol%, branching structure is inadequate. In exceeding ten-mol %, there is an inclination for the branching reaction by chain transfer to increase and to cause gelation.

[0021] moreover -- the case where the (D) component is used -- the total mol sum of (A) - (D) component -- receiving -- usually -- or less about 40 mol % -- it is used less than [ 30 mol % ] preferably. (D) When a component exceeds 40-mol %, it is difficult to get in sufficient paper durability effectiveness. in addition -- the case where anionic is given to a copolymer as a (D) component -- said total mol sum -- receiving -- usually -- an anionic vinyl monomer -- 1 - 20-mol % -- desirable -- 2 - 15-mol % -- it is used. the case where cationicity is given to a copolymer -- the total mol sum -- receiving -- usually -- a cationic vinyl monomer -- 1-20-mol % -- desirable -- 2-15-mol % -- it is used. moreover -- the case where both sexes are given to a copolymer -- the total mol sum -- receiving -- usually -- an anionic vinyl monomer -- 1-15-mol % -- desirable -- a 2-10-mol % and cationic vinyl monomer -- 1-15-mol % -- desirable -- 2-10-mol % -- it is used.

[0022] Composition of the copolymer used for this invention can be conventionally performed by various well-known approaches. For example, said various monomers ((A) - (C) component or (A) - (D) component) and water can be taught to a predetermined reaction container, a radical polymerization initiator can be added, and the water-soluble acrylamide (meta) system copolymer made into the purpose by warming under churning can be obtained. Reaction temperature is about 50-100 degrees C, and reaction time is usually about 1 - 5 hours. Reaction concentration (monomer concentration) can usually be performed at about 10 - 40 % of the weight, and can carry out a polymerization also in high concentration. Moreover, without diluting also in a high-concentration case, it can be used and the water solution of the obtained copolymer can be saved. In addition, an approach to teach a monomer can be performed by the various approaches that a coincidence polymerization, a continuation dropping polymerization, etc. are conventionally well-known. As a radical polymerization initiator, the usual radical polymerization initiators, such as a redox system polymerization initiator of the form which combined persulfate, such as potassium persulfate and ammonium persulfate, or these and the reducing agent like a sodium

hydrogensulfite, can be used. Moreover, an azo system initiator may be used together to said radical polymerization initiator. the amount of the radical polymerization initiator used -- 0.05- of the AUW sum of a monomer -- it is 0.1 - 0.5 % of the weight preferably 2.0% of the weight. At 0.05 % of the weight, when the polymerization itself does not fully advance but it crosses 2.0 % of the weight of another side, it is difficult to obtain the amount polymer of macromolecules.

[0023] Weight average molecular weight is 500,000 to about 6 million, and can usually use the acrylamide (meta) system copolymer obtained in this way as various kinds of additives for paper manufacture, such as a layer indirect arrival agent of \*\*\*\*\* and \*\*\*\* doubling paper, outside internal chemicals, such as a filtration improvement agent and a paper reinforcing agent, a surface paper reinforcing agent, etc. In addition, when using as a layer indirect arrival agent of internal chemicals, such as a filtration improvement agent and a paper reinforcing agent, and \*\*\*\* doubling paper etc., it is desirable that weight average molecular weight is 2 million or more. Moreover, viscosity is good to usually use about (25 degrees C) 10000cps by the following descriptions from the point of handling nature. In addition, although the additive for paper manufacture of this invention is adjusted to 10 - 40 % of the weight of solid content concentration, it can adjust about (25 degrees C) 10000cps of viscosity for solid content concentration to 40% of the weight of a case below. Thus, although the additive for paper manufacture which comes to contain the acrylamide (meta) system copolymer of this invention is the amount of macromolecules, it is hypoviscosity and can be used by high solid content concentration.

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EXAMPLE

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[Example] Hereafter, an example and the example of a comparison are given and this invention is explained more concretely. In addition, each of sections and %s is based on weight criteria, as long as there is no special mention.

[0026] The acrylamide 234.6 section (it is the same as that below of 95 below [ % and ] to the total mol sum of a monomer), the meta-allyl compound sulfonic-acid soda 16.5 section (three-mol %), the dimethyl acrylamide 6.9 section (two-mol %), and the ion-exchange-water 960 section (21% of monomer concentration) were taught to the 4 opening flask equipped with example 1 agitator, a thermometer, a reflux cooling pipe, and nitrogen gas installation tubing, and the oxygen in the system of reaction was removed through nitrogen gas. The inside of a system was made into 40 degrees C, and the ammonium persulfate 0.25 section and the sodium-hydrogensulfite 0.15 section were supplied as a polymerization initiator to the bottom of churning. It was kept warm for 2 hours, after carrying out a temperature up to 90 degrees C. The ion-exchange-water 70 section (it adjusts to 20% of solid content concentration) was supplied after polymerization termination, pH4.5, 20.2% of solid content, and viscosity (25 degrees C) obtained 9800cps, and weight average molecular weight obtained the copolymer water solution of 2,900,000. Moreover, it was 0% when the amount of gels was measured. In addition, although the amount of gels does not pass this filter when filtering a sample with a 0.45-micrometer membrane filter, it means a content (% of the weight).

[0027] In examples 2-11 and one to example of comparison 5 example 1, as shown in Table 1, even if few [ either ] among the class of (A) - (D) component, or its operating rate, one sort was changed, and also the same actuation as an example 1 was performed, and various copolymer water solutions were obtained. the description of the obtained various copolymer water solutions -- a value is shown in Table 2. In addition, in the example 10, the polymerization was performed at 41% of monomer concentration, and after polymerization termination, ion exchange water was thrown in so that it might become 40% of solid content concentration. Moreover, in the examples 4 and 5 of a comparison, it carried out by adding isopropyl alcohol.

[0028]

[Table 1]



	モノマーの種類および使用割合（モル％）											
	(A) 成分		(B) 成分		(C) 成分		(D) 成分			その他		
							アニオン	カチオン	ニオン			
実施例 1	AM	95	SMAS	3	DMAA	2	—	—	—			
実施例 2	AM	90	SMAS	3	DMAA	2	AA	5	—			
実施例 3	AM	90	SMAS	3	DMAA	2	—	DM	5			
実施例 4	AM	89	SMAS	3	DMAA	2	AA	3	DM	3		
実施例 5	AM	85	SMAS	3	DMAA	2	—	—	AN10			
実施例 6	AM	89	SMAS	3	IPAA	2	AA	3	DM	3		
実施例 7	AM	89	SAS	3	DMAA	2	AA	3	DM	3		
実施例 8	AM	89	SAS	3	IPAA	2	AA	3	DM	3		
実施例 9	AM	87	SAS	5	IPAA	2	AA	3	DM	3		
実施例10	AM	85	SAS	7	IPAA	2	AA	3	DM	3		
実施例11	AM	90	SAS	2	DMAA	2	IA	3	DM	3		
比較例 1	AM	90.5	SMAS	3	—	—	AA	3	DM	3	AMA	0.5
比較例 2	AM	90.8	SMAS	3	—	—	AA	3	DM	3	TAIC	0.2
比較例 3	AM	89	SMAS	3	—	—	AA	3	DM	3	N-MAA	2
比較例 4	AM	92	—	—	DMAA	2	AA	3	DM	3	IPA	5
比較例 5	AM	92	—	—	DMAA	2	IA	3	DM	3	IPA	3

[0029] Front Naka, AM:acrylamide, SMAS:meta-allyl-compound sulfonic-acid soda, SAS:allyl-compound sulfonic-acid soda, DMAA:N,N-dimethylacrylamide, IPAA:N-isopropyl acrylamide, AA:acrylic acid, IA:itaconic acid, DM:dimethylaminoethyl methacrylate, AMA:allyl-compound methacrylate, TAIC:triallyl isocyanurate, N-MAA:N-methoxy acrylamide, IPA: Express isopropyl alcohol.

[0030]

[Table 2]

	性 状				
	pH	固形分 (%)	粘度 (c p s)	重量平均分子量	ゲル量 (%)
実施例 1	4. 5	20. 2	9 8 0 0	$290 \times 10^4$	0
実施例 2	4. 2	20. 5	9 3 0 0	$270 \times 10^4$	0
実施例 3	4. 7	20. 4	8 9 0 0	$325 \times 10^4$	0
実施例 4	4. 5	20. 5	9 5 0 0	$310 \times 10^4$	0
実施例 5	4. 3	20. 8	9 9 0 0	$250 \times 10^4$	0
実施例 6	4. 5	20. 2	9 1 0 0	$275 \times 10^4$	0
実施例 7	4. 4	20. 5	9 3 0 0	$285 \times 10^4$	0
実施例 8	4. 5	20. 8	9 6 0 0	$280 \times 10^4$	0
実施例 9	4. 5	20. 5	9 3 0 0	$280 \times 10^4$	0
実施例 10	4. 5	40. 2	9 5 0 0	$520 \times 10^4$	0
実施例 11	4. 0	20. 5	8 0 0 0	$300 \times 10^4$	0
比較例 1	4. 6	20. 3	9 1 0 0	$220 \times 10^4$	15
比較例 2	4. 5	20. 5	9 5 0 0	$240 \times 10^4$	20
比較例 3	4. 5	20. 2	7 8 0 0	$185 \times 10^4$	0
比較例 4	4. 7	20. 3	7 3 0 0	$170 \times 10^4$	0
比較例 5	4. 2	20. 3	9 0 0 0	$220 \times 10^4$	0

[0031] Beating is carried out with a beater. (The performance-evaluation approach 1) corrugated paper used paper -- a Niagara style -- Add a sulfuric-acid band 1.6% to the pulp adjusted to Canadian standard freeness (C. S.F) 420ml, and it is referred to as pH5.5. Subsequently, 0.6% for pulp is added by making into a paper reinforcing agent each copolymer water solution obtained in examples 1-11 or the examples 1-5 of a comparison. After agitating, pulp slurry concentration is diluted so that it may become 0.1%, and it is basis-weight 150 g/m<sup>2</sup> with the TAPPI sheet machine. Paper making is carried out so that it may become, and it is 2 5kg/cm. Press dehydration was carried out for 2 minutes. after [ subsequently, / JIS ] drying for 3 minutes in 105 degrees C with a rotation mold dryer and carrying out gas conditioning to the bottom of the condition of 20 degrees C and 65%R.H. for 24 hours P 8112 -- applying correspondingly -- a ratio -- bursting strength was measured. A result is shown in Table 3.

[0032] (The performance-evaluation approach 2) N-BKP -- a Niagara style -- each copolymer water solution obtained in each above-mentioned example and the example of a comparison by the pulp (pH6.8) which carried out beating with the beater, and which was adjusted to 550 (C. S.F)ml -- the above -- the same -- adding -- the same actuation as the above -- carrying out -- a ratio -- bursting strength was measured. A result is shown in Table 3.

[0033]

[Table 3]

	評価方法 1	評価方法 2
実施例 1	2. 5 5	5. 8 0
実施例 2	2. 6 0	5. 8 5
実施例 3	2. 6 3	5. 8 9
実施例 4	2. 7 0	5. 9 6
実施例 5	2. 6 4	5. 9 0
実施例 6	2. 6 8	5. 9 3
実施例 7	2. 6 7	5. 9 1
実施例 8	2. 6 8	5. 9 5
実施例 9	2. 6 9	5. 9 6
実施例 10	2. 5 1	5. 7 3
実施例 11	2. 6 3	5. 8 3
比較例 1	2. 4 5	5. 5 8
比較例 2	2. 4 0	5. 5 2
比較例 3	2. 3 7	5. 4 8
比較例 4	2. 3 5	5. 5 0
比較例 5	2. 4 0	5. 4 2

[0034] From the result of Table 3, it is admitted that the additive for paper manufacture using the acrylamide system copolymer obtained by this invention discovers the outstanding paper durability enhancing effect.

[0035] In examples 12-17 and example of comparison 6 example 1, as shown in Table 4, even if few [ either ] among the class of (A) - (D) component, or its operating rate, one sort was changed, and also the same actuation as an example 1 was performed, and various copolymer water solutions were obtained. the description of the obtained various copolymer water solutions -- a value is shown in Table 5. In addition, in each example and the example of a comparison, the polymerization was performed at 21% of monomer concentration, 31%, or 41%, and ion exchange water was thrown in after polymerization termination, and it prepared so that it might become the solid content concentration (20%, 30%, or about 40%) shown in Table 5.

[0036]

[Table 4]

	モノマーの種類および使用割合 (モル%)						
	(A) 成分	(B) 成分	(C) 成分	(D) 成分			その他
				アニオン	カチオン	ノニオン	
実施例12	AM 93.5	SMAS 0.5	DMAA 1	IA 5	--	--	
実施例13	AM 68	SMAS 1	DMAA 1	AA 5	--	AN25	
実施例14	AM 93	SMAS 2	DMAA 1	--	DM 5	--	
実施例15	AM 83	SMAS 1	DMAA 1	IA 5	--	AN10	
実施例16	AM 87	SMAS 2	DMAA 1	IA10	--	--	
実施例17	AM 62	SMAS 2	DMAA 1	AA 5	--	AN30	
比較例 6	AM 68.5	SMAS 1	---	AA 5		AN25	AMA 0.5

[0037] Front Naka, AM:acrylamide, SMAS:meta-allyl-compound sulfonic-acid soda, DMAA:N,N-dimethylacrylamide, IA:itaconic acid, AA:acrylic acid, DM:dimethylaminoethyl methacrylate, AN:acrylonitrile, AMA: Express allyl compound methacrylate.

[0038]

[Table 5]

	性 状				
	pH	固形分 (%)	粘度 (c p s)	重量平均分子量	ゲル量 (%)
実施例12	5. 5	30. 8	8500	$131 \times 10^4$	0
実施例13	5. 3	30. 0	9200	$100 \times 10^4$	0
実施例14	4. 7	20. 5	9900	$182 \times 10^4$	0
実施例15	5. 1	30. 7	4700	$156 \times 10^4$	0
実施例16	5. 3	40. 2	9300	$122 \times 10^4$	0
実施例17	5. 2	40. 4	4100	$93 \times 10^4$	0
比較例 6	5. 5	30. 0	12000	$170 \times 10^4$	15

[0039] (The performance-evaluation approach 3) Lab size press coating equipment (Kumagai Riki Kogyo make) was used for high-quality acid paper (basis-weight 60 g/m<sup>2</sup>), and after it carried out coating (a part for 40m/in 2% of coating concentration, nip pressure 15 kg/cm, and coating rate), having used as the paper reinforcing agent each copolymer water solution obtained in examples 10-16 or the examples 5-6 of a comparison, it dried for 1 minute at 105 degrees C using the rotation dryer. After desiccation, after carrying out gas conditioning to the bottom of the condition of 20 degrees C and 65%R.H. for 24 hours, RI printing testing machine (product made from \*\*\*\*\*) performed the surface strength test using the nip pressure of 4mm, and SMX ink (the TOYO INK MFG. CO., LTD. make, tuck 20), and the picking condition after printing was observed with the naked eye. 5 was made into good and it considered as five-step evaluation by making 1 into wrong. A result is shown in Table 6.

[0040] (The performance-evaluation approach 4) It is J.TAPPI about the interior reinforcement (Kgf-cm) after carrying out gas conditioning like the performance-evaluation approach 3. It

measured according to No.54. A result is shown in Table 6.

[0041]

[Table 6]

	評価方法 3	評価方法 4
実施例12	4. 9	2. 5 6
実施例13	4. 4	2. 5 3
実施例14	4. 7	2. 5 5
実施例15	4. 7	2. 5 5
実施例16	4. 9	2. 5 4
実施例17	4. 4	2. 5 5
比較例 6	4. 1	2. 4 5

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[Translation done.]